

SUPPORT FOR THE AMENDMENT

Claims 1, 3-5, and 9 have been amended.

The amendment of Claims 1, 3-5, and 9 is supported by the corresponding previously pending claims, as well as page 21, lines 3-14.

No new matter is believed to have been added by these amendments.

REMARKS

Claims 1-20 are active in the present application.

At the outset, Applicants wish to acknowledge Examiner Weiner for the helpful and courteous discussion with their undersigned Representative on August 13, 2003. The content of this discussion is reflected in the comments and amendments set forth herein. Applicants would also like to thank Examiner Weiner for the indication that the species 2,6-di-tert-butyl-4-methylpyridine and Claims 17-18 are allowable.

Favorable reconsideration and allowance of the claims is solicited.

The rejection of Claims 1-9, 11-13, and 19 under 35 U.S.C. §102(b) over the Iwakura et al is obviated by amendment.

The Examiner asserts that Iwakura et al disclose a battery comprising a cathode containing Li or Li alloy, an anode containing Mo dioxide, V pentoxide, and Li as anode active component and an electrolyte liquid. The Examiner further asserts that Iwakura et al disclose that the electrolyte contains pyridine or a pyridine derivative where R<sup>1</sup> to R<sup>5</sup> is H or an alkyl group.

Although Iwakura et al may recite a pyridine derivative (see Claim 1), Applicants note that the pyridine derivatives disclosed in this references are distinct from the claimed pyridine derivatives. Specifically, Iwakura et al only pyridine substituted with an alkyl group having 2 or less carbon atoms, whereas the proviso of the presently claimed invention specifies that when R<sup>1</sup> to R<sup>5</sup> are a hydrogen or an alkyl, at least one of R<sup>1</sup> to R<sup>5</sup> is an alkyl group having 4 or more carbon atoms.

For the Examiner's convenience, Applicants note that Iwakura et al only illustrate the following pyridine derivatives:

- trimethylpyridine (the largest carbon number of the substituents is one),
- methylpyridine (the largest carbon number of the substituent is one),
- ethylpyridine (the largest carbon number of the substituent is two),
- diethylpyridine (the largest carbon number of the substituents is two),
- methylethylpyridine (the largest carbon number of the substituents is two), and
- dimethylethylpyridine (the largest carbon number of the substituents is two).

In fact, the working example Iwakura et al utilizes dimethylpyridine (the largest carbon number of the substituents is one). In contrast, in the present invention, when all of R<sup>1</sup> to R<sup>5</sup> are a hydrogen atom or an alkyl group having 1 to 20 carbon atoms, at least one of the alkyl groups has 4 more carbon atoms. Further, the invention of Iwakura et al is characterized by obtaining effect of improving cycle characteristics of battery. Iwakura et al neither describes nor suggests that an alkyl group having specific carbon number is selected like the present invention and that the effect of improving high-temperature characteristics of battery is obtained by the selection of the alkyl group having specific carbon number, at all.

The standard for determining anticipation requires that the reference “must teach every element of the claim” (MPEP §2131). For the reasons set forth above, Iwakura et al fail to meet this standard. Therefore, the anticipation rejection over Iwakura et al is no longer tenable.

Moreover, Applicants submit that Iwakura et al cannot even serve as the basis for a *prima facie* case of obviousness. The Federal Circuit has defined the parameters that may be considered in determining the proper use of chemical structure as the basis for obviousness rejections under 35 U.S.C. §103 in *In re Jones*, 21 USPQ2d 1941 (Fed. Cir. 1992) (copy enclosed). The court cited the following examples of relationships that have given rise to a *prima facie* case of obviousness:

triorthoesters and tetraorthoesters;

stereoisomers;

adjacent homologs and structural isomers; and

acid and ethyl ester (*Id.*, at 1943).

In the present case, there exists no motivation to modify the compounds disclosed by Iwakura et al to obtain the claimed pyridine compounds because Iwakura et al is silent in this regard and because the relationship between the claimed compounds and those disclosed by Iwakura et al fail to satisfy any of the above-mentioned relationships to be defined as homologs by the Federal Circuit.

In view of the foregoing, withdrawal of this ground of rejection is requested.

The rejection of Claims 1-9, 12-16, and 19 under 35 U.S.C. §102(b) over the Tsutsumi et al is obviated by amendment.

Tsutsumi et al disclose an electrolytic solution for a lithium secondary battery having an electrolyte; an organic solvent; and an additive, wherein the additive is an aromatic nitrogen-containing heterocyclic compound such as pyrazine, quinoxaline, indole, phenazine, phthalazine, pyrimidine, or a mixture thereof (Abstract).

In the compound represented by the general formula (I) as recited in claim 1 and in column 2, lines 8-28 of Tsutsumi et al, the substituents of the pyridine derivatives are limited to a lower alkyl group having 1 to 3 carbon atoms. This disclosure is distinct from that of the present invention. Further, examples of substituents other than the alkyl group in Tsutsumi et al include a halogen atom, phenyl group and hydroxyl group. However, regarding the halogen atom, Tsutsumi et al only disclose that "examples of the halogen atoms include chlorine atom and bromine atom" in column 3, line 2. In contrast, in the present invention, an example of the substituent includes fluoro group. Further, Tsutsumi et al disclose, as an example of the substituent, phenyl group, but does not illustrate any specific example. The present invention

sets for that when  $R^1$  to  $R^5$  independently represent a phenyl group, two or more of  $R^1$  to  $R^5$  represent phenyl groups. In other words, when a phenyl group is present in the claimed pyridine derivative, there are at least two phenyl groups.

Further, the invention of Tsutsumi et al is characterized by obtaining effect of improving cycle characteristics of battery. Tsutsumi et al neither disclose nor suggest that the effect of improving high-temperature characteristics of battery is obtained by an alkyl group having specific carbon number like the present invention, at all.

Therefore, under the standard for determining anticipation under MPEP §2131 and the obviousness test set forth in *In re Jones (supra)*, Applicants submit that the present invention is neither anticipated by nor obvious in view of Tsutsumi et al.

Withdrawal of this ground of rejection is requested.

The rejection of Claims 1-9, 12-16, 19-20 under 35 U.S.C. §102(b) over Suemori et al is obviated by amendment.

The Examiner asserts that Suemori et al disclose a battery comprising a positive electrode, a negative electrode made of a carbon-based material, and a non-aqueous electrolytic solution containing pyridine or a pyridine derivative. Applicants note that although Claim 1 of Suemori et al recites pyridine or a pyridine derivative, the compound recited in claim 2 or described in the detailed description clearly is only picoline substituted with an alkyl group having one carbon atom.

Further, Suemori et al discloses: "Examples of pyridine derivatives include alkylpyridines a hydrogen atom at an ortho, meta or para position of the pyridine moiety of which is substituted with an alkyl group having 1 to 3 carbon atoms, etc." (see paragraph [0006]). In contrast, in the present invention, when all of  $R^1$  to  $R^5$  are a hydrogen atom or an alkyl group having 1 to 20 carbon atoms, at least one of the alkyl groups has 4 more carbon

atoms. Accordingly, the pyridine derivative as described in Suemori et al is clearly different from the compound according to the present invention.

Moreover, the invention of Suemori et al is characterized by obtaining effect of improving cycle characteristics of battery. Suemori et al neither disclose nor suggest that an alkyl group having specific carbon number is selected like the present invention and that the effect of improving high-temperature characteristics of battery is obtained by the selection of the alkyl group having specific carbon number.

In view of the foregoing, under the standard for determining anticipation under MPEP §2131 and the obviousness test set forth in *In re Jones (supra)*, Applicants submit that the present invention is neither anticipated by nor obvious in view of Tsutsumi et al.

Withdrawal of this ground of rejection is requested.

The rejections of Claim 10 under 35 U.S.C. §102(b) and/or under 35 U.S.C. §103(a) over Iwakura et al, Tsutsumi et al, or Seumori et al are obviated by amendment.

Iwakura et al, Tsutsumi et al, and Seumori et al are discussed above with respect to Claim 1. As stated above, Claim 1 is neither anticipated by nor obvious in view of Iwakura et al, Tsutsumi et al, or Seumori et al. Claim 10 depends directly from Claim 1; therefore, for the same reasons set forth above for Claim 1, Claim 10 is not anticipated by or obvious in view of the disclosures of Iwakura et al, Tsutsumi et al, and Seumori et al.

Applicants request withdrawal of these grounds of rejection.

The rejection of Claims 7-8 and 10 under 35 U.S.C. §112, second paragraph, is traversed.

With respect to Claims 7 and 8, the Examiner has taken the position that the phrase "aforesaid substituents" is unclear. Applicants note that Claims 7 and 8 depend directly from

Claim 1; therefore, the artisan would readily understand that the phrase “aforesaid substituents” refers to the substituents recited in Claim 1. Namely this phrase would include the following definition for the recited substituents:  $R^1$  to  $R^5$  independently represents a hydrogen atom or a substituent composed of an alkyl group having 1 to 20 carbon atoms, an alkenyl group having 2 to 20 carbon atoms, an alkoxy group having 1 to 4 carbon atoms, an aryloxy group having 6 to 10 carbon atoms, a dialkylamino group having 2 to 8 carbon atoms, a 3-thienyl group, a cyano group, a fluoro group, an alkoxycarbonyl group having 1 to 6 carbon atoms, an arylcarbonyl group having 6 to 10 carbon atoms, an alkylcarbonyl group having 1 to 12 carbon atoms, a cyanoalkyl group having 1 to 4 carbon atoms, an alkoxycarbonylalkyl group having 3 to 13 carbon atoms, a pyrrol-1-ylmethyl group, a 1-pyrrolidinyl group, a 1-piperidino group, a phenyl group, a 1H-pyrrol-1-yl group, an alkoxyalkyl group having 2 to 12 carbon atoms, a dialkylaminoalkyl group having 3 to 18 carbon atoms, an aryloxy group having 6 to 10 carbon atoms, an arylalkyl group the aryl moiety of which has 6 to 10 carbon atoms and the alkyl moiety of which has 2 to 6 carbon atoms, an isothiocyano group, a dialkylaminocarbonyl group having 2 to 8 carbon atoms, a 5-oxazole group, a trifluoromethyl group, a 1-pyrrolidine-2,5-dione group, a 1H-pyrrol-1-ylalkyl group having 1 to 6 carbon atoms, a 4,5-dihydro-oxazol-2-yl group, a 1,3,4-oxadiazol-2-yl group, a nitro group, a 1-piperidinyl group, a 1-alkylpyrrol-2-yl group having 1 to 6 carbon atoms, a 4-1,2,3-thiadiazole group, a 2-1,3,4-oxadiazole group, a morpholino group and a 1-pyrrolin-2-yl group, with the recited provisos (see Claim 1).

Regarding Claim 10, the Examiner has taken the position that the phrase “calculated according to ab initio method... the adduct between the pyridin compound and hydrofluoric acid...” is unclear. Not only does the claim provide all the context necessary to reasonably convey the scope of the claim with sufficient clarity, Applicants offer the following additional comments. Moreover, as evidence that the ab initio method would be well

appreciated by the skilled artisan, Applicants **enclose herewith** Hehre et al, "Ab Initio Molecular Orbital Theory", John Wiley & Sons. Inc. New York 1986 ISBN 0-47X-81241-2, for the Examiner's reference.

The ab initio method is a method of molecular orbital calculation that is widely used in molecular quantum mechanics and is a method of quantitatively calculating chemical phenomena by strictly solving Schrodinger partial differential equation without using the experimental value. (see page 1, line 14, Prologue) Gaussian 94 is the name of a commercially available program (maker: Gaussian Inc.) for ab initio calculations.

Generally, a wave function expressing a molecule is represented by a product of molecular orbital, and the molecular orbital is represented by a combination of functions called basis set (base set) (see page 7, line 4). The precision of calculation varies depending upon a kind of "base set" to be used, and in claim 10, 3-21G is selected as "base set".

In claim 10, energy value of a pyridine compound is obtained via working of obtaining the most stable structure of the pyridine compound using Gaussian 94 based on the ab initio method. Similarly, the energy value of hydrofluoric acid and the energy value of adduct in a state of bonding pyridine compound and hydrofluoric acid are obtained. Using such values, the energy value of adduct is subtracted from sum of (the energy value of pyridine compound) and (the energy value of hydrofluoric acid) to obtain bonding energy of pyridine compound and hydrofluoric acid.

In view of the foregoing, Applicants believe that the language of the claims are such that a person of ordinary skill in the art could interpret the metes and bound of the claims so as to understand how to avoid infringement (MPEP §2173.02). Applicants note that this rejection appears to be because the Examiner merely wants the Applicant to improve the clarity or precision of the language used. However, since the skilled artisan can readily



appreciate the meaning of the claims, Applicants submit that further amendments are unnecessary. Therefore, Applicants request withdrawal of the claim objections pursuant to MPEP §2173.02.

Acknowledgement that this ground of rejection has been withdrawn is requested.

Applicants submit that the present application is now in condition for allowance. Early notification of such action is earnestly solicited.

Respectfully submitted,

OBLON, SPIVAK, McCLELLAND,  
MAIER & NEUSTADT, P.C.



Norman F. Oblon  
Attorney of Record  
Registration No. 24,618

Vincent K. Shier, Ph.D.  
Registration No. 50,552



22850

Tel.: 703-413-3000  
Fax: 703-413-3220  
NFO:VKS

This Page Is Inserted by IFW Operations  
and is not a part of the Official Record

## **BEST AVAILABLE IMAGES**

Defective images within this document are accurate representation of  
The original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

---

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning documents *will not* correct images,  
please do not report the images to the  
Image Problem Mailbox.**

In re Jones (CA FC) 21 USPQ2d 1941

**In re Jones**

**U.S. Court of Appeals Federal Circuit  
21 USPQ2d 1941**

**Decided February 28, 1992  
No. 91-1380**

**Headnotes**

**PATENTS**

**1. Patentability/Validity -- Obviousness -- Relevant prior art -- Particular inventions  
(§ 115.0903.03)**

Claimed novel salt of acid commonly known as "dicamba" is not so closely related in structure to substituted ammonium salts disclosed in prior patent as to be prima facie obvious, since claimed salt is primary amine with ether linkage, whereas diethanolamino salt disclosed in reference patent is secondary amine without ether linkage, since claimed salt is plainly acyclic or linear, whereas morpholino salt, which is only substituted ammonium salt of dicamba with ether linkage disclosed in reference patent, is cyclic in structure, and since isopropylamino salt disclosed in reference patent is primary amine, but has iso-structure quite different from that of claimed salt.

**2. Patentability/Validity -- Obviousness -- Relevant prior art -- Particular inventions  
(§ 115.0903.03)**

Claimed novel salt of acid commonly known as "dicamba" cannot be held prima facie obvious in

view of salts disclosed in prior patent, even though claimed salt is member of genus of substituted ammonium salts broadly disclosed in reference patent, since reference discloses potentially infinite genus of "substituted ammonium salts" of dicamba, and lists several such salts, but does not specifically disclose salt claimed in application, and since claimed salt is not sufficiently similar to those disclosed in reference as to render it prima facie obvious.

**3. Patentability/Validity -- Obviousness -- Combining references (§ 115.0905)**

Contention that one skilled in herbicidal art would have been motivated to use, with acid commonly known as "dicamba," substituted ammonium salt such as that disclosed in two prior references does not warrant holding that claimed substituted ammonium salt of dicamba for use as herbicide is prima facie obvious, since there is no suggestion for combining disclosures of those references either in references themselves, which are directed to shampoo additives and production of morpholine, respectively, or in knowledge generally available to those skilled in art.

**Case History and Disposition:**

Page 1941

Appeal from the U.S. Patent and Trademark Office, Board of Patent Appeals and Interferences.

Patent application of Rita S. Jones, Michael T. Chirchirillo and Johnny L. Burns, serial no. 07/099,279 (the 2-(2'-aminoethoxy)-ethanol salt of dicamba). From decision upholding rejection of only claim in application, applicants appeal. Reversed.

**Attorneys:**

Melvyn M. Kassenoff, East Hanover, N.J. (Gerald D. Sharkin and Richard E. Villa, East Hanover; Joanne M. Giesser, Palo Alto, Calif., with him on brief), for appellant.

Harris A. Pitlock, associate solicitor (Fred E. McKelvey, solicitor, with him on brief; Richard E. Schafer, of counsel), for appellee.

Page 1942

**Judge:**

Before Rich, Archer, and Clevenger, circuit judges.

**Opinion Text**

**Opinion By:**

Rich, J.

Rita S. Jones et al. (collectively Jones) appeal from the April 15, 1991 decision of the Patent and Trademark Office (PTO) Board of Patent Appeals and Interferences (Board), Appeal No. 90-1920, sustaining the rejection of claim 1, the only claim of application Ser. No. 07/099,279, titled "The 2-(2'-Aminoethoxy) -- Ethanol Salt of Dicamba," as unpatentable under 35 USC 103. We conclude that the PTO has not presented a *prima facie* case of obviousness, and therefore *reverse*.

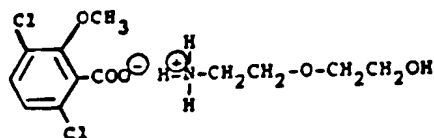
**The Invention**

The Claimed invention is a novel salt of 2-methoxy-3, 6-dichlorobenzoic acid, which acid is commonly referred to as "dicamba." A known herbicide, dicamba has typically been sold in the form of its known dimethylamine salt.

The sole claim of the application on appeal reads:

1. The 2-(2'-aminoethoxy) ethanol salt of dicamba.

The claimed salt has the following structure:



**The Rejection**

Claim 1 stands rejected as obvious in view of the combined teachings of the following references:

Richter, U.S. Patent No. 3,013,054, Dec. 12, 1961

Moyle et al., U.S. Patent No. 3,056,669, Oct. 2, 1962

Balassa, U.S. Patent No. 3,725,031, Apr. 3, 1973

Zorayan et al., 88 *Chem. Abstracts* No. 52300j, 1978

Wideman, 86 *Chem. Abstracts* No. 43711a, 1977

Richter, which all agree is the closest prior art, discloses dicamba in free acid, ester, and salt forms, for use as a herbicide. Among the salt forms disclosed are substituted ammonium salts, a

genus which admittedly encompasses the claimed salt. Richter does not specifically disclose the claimed 2-(2'-aminoethoxy) ethanol salt, however. Most notably, Richter discloses (emphasis and bracketed word ours):

Compositions in which X is substituted ammonium are amine salts of 2-methoxy-3, 6-dichlorobenzoic acid [dicamba] and are prepared by the addition of the free acid to various amines. Typical amines which can be used to prepare such amine salts are dimethylamine, trimethylamine, triethylamine, diethanolamine, triethanolamine, isopropylamine, morpholine, and the like. *The resulting products are, respectively, the dimethylamino, trimethylamino, triethylamino, diethanolamino, triethanolamino, isopropylamino, and morpholino salts of 2-methoxy-3, 6-dichlorobenzoic acid.*

Zorayan teaches the amine (H [inf 2] N (CH [inf 2] CH [inf 2] O) [inf 2] H) used to make the claimed salt, as well as the use of that amine in the preparation of surfactants for shampoos, bath preparations, and emulsifiers.

Wideman also teaches the amine disclosed in Zorayan.

The content of the remaining references is unnecessary to our decision.

The Board upheld the examiner's rejection of claim 1 as obvious, finding that the claimed 2-2'-aminoethoxy) ethanol salt of dicamba and the diethanolamine salt of dicamba specifically disclosed by Richter were "closely related in structure," and that based upon the expectation that "compounds similar in structure will have similar properties," a *prima facie* case of obviousness had arisen. The Board found that Jones' rebuttal evidence (Rule 132 declarations and data reported in the specification) failed to "compare the claimed subject matter with the closest prior art," and accordingly did not serve to rebut the *prima facie* case. This appeal followed.

### Analysis

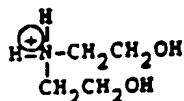
The Solicitor contends that the claimed salt falls within the genus of substituted amine salts of dicamba disclosed by Richter, and that, like Richter's genus, the claimed compound has herbicidal activity. Thus, the Solicitor urges, under the circumstances of this case, (1) the genus/species relationship and (2) the common utility of the claimed and prior art compounds support the Board's holding of *prima facie* obviousness. Moreover, the Solicitor adds, although the claimed compound is neither a homolog nor a position isomer of those salts specifically disclosed in Richter, it is structurally similar thereto, particularly the diethanolamino salt noted by the Board.

Page 1943

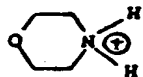
The question of "structural similarity" in chemical patent cases has generated a body of patent law unto itself. 1 Particular types or categories of structural similarity without more have, in past cases, given rise to *prima facie* obviousness; see, e.g., *In re Dillon*, 919 F.2d 688, 692-94, 16 USPQ2d 1897, 1900-02 (Fed. Cir. 1990) (tri-orthoesters and tetra-orthoesters), *cert. denied*,

\_\_\_\_ U.S. \_\_\_\_, 111 S. Ct. 1682 (1991); *In re May*, 574 F.2d 1082, 197 USPQ 601 (CCPA 1978) (stereoisomers); *In re Wilder*, 563 F.2d 457, 195 USPQ 426 (CCPA 1977) (adjacent homologs and structural isomers); *In re Hoch*, 428 F.2d 1341, 166 USPQ 406 (CCPA 1970) (acid and ethyl ester). However, none of these types of structural similarity are involved here. And in any event, this court has previously stated that generalization is to be avoided insofar as specific structures are alleged to be *prima facie* obvious one from the other. *In re Grabiak*, 769 F.2d 729, 731, 226 USPQ 870, 872 (Fed. Cir. 1985).

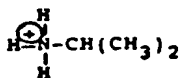
[1] On the basis of the record before us, we cannot sustain the Board's conclusion that the claimed salt and the diethanolamino salt disclosed by Richter are so "closely related in structure" as to render the former *prima facie* obvious in view of the latter. The claimed salt is a primary amine with an ether linkage. The diethanolamino salt disclosed by Richter is a secondary amine, without an ether linkage:



In addition, the only substituted ammonium salt of dicamba expressly disclosed by Richter having an ether linkage is the morpholino salt, which is *cyclic* in structure:



The claimed salt is, plainly, *a* cyclic; i.e., linear. Lastly, while the isopropylamino salt disclosed by Richter is a primary amine, as is the claimed salt, its iso- structure is quite different:



[2] The lack of close similarity of structure is not negated by the fact that the claimed salt is a member of Richter's broadly disclosed genus of substituted ammonium salts of dicamba. The Solicitor contends that "[t]he relative size of the genus disclosed by the prior art would not appear to be a controlling factor in determining whether a *prima facie* case of obviousness exists for a species encompassed within the described genus," citing *Merck & Co. v. Biocraft Labs., Inc.*, 874 F.2d 804, 806-09, 10 USPQ2d 1843, 1845-48 (Fed. Cir.), *cert. denied*, \_\_\_\_ U.S. \_\_\_\_, 110 S. Ct. 498 (1989). We decline to extract from *Merck* the rule that the Solicitor appears to suggest -- that regardless of how broad, a disclosure of a chemical genus renders obvious any species that happens to fall within it. In *Merck*, at issue on appeal was whether claims to a composition of two diuretics, amiloride and hydrochlorothiazide, present in a particular "medically synergistic" weight ratio, would have been obvious in view of a specific prior art disclosure of amiloride in combination with hydrochlorothiazide, one of 1200 such combinations disclosed in the prior art reference. *Id.* at 806, 10 USPQ2d at 1845. Based on the facts before it, including evidence at trial that the experimentation needed to arrive at the claimed dosage was "nothing more than routine," *Id.* at 809, 10 USPQ2d at 1847, the court affirmed the trial court's determination of obviousness. In contrast, though Richter discloses the potentially infinite genus of "substituted ammonium salts" of dicamba, and lists several such

salts, the salt claimed here is not specifically disclosed. Nor, as we have explained above, is the claimed salt sufficiently similar in structure to those specifically disclosed in Richter as to render it *prima facie* obvious. Every case, particularly those raising the issue of obviousness under section 103, must necessarily be decided upon its own facts.

[3] The Solicitor points out that, given the breadth of forms of dicamba (free acid, ester, or salt) disclosed by Richter as having herbicidal utility, one of ordinary skill in the art would appreciate that the dicamba group has significance with respect to imparting herbicidal activity to dicamba compounds. Thus, the Solicitor contends, one skilled in the art would have been motivated to use, with dicamba, substituted ammonium salts made from a known amine, such as the amine disclosed by Zorayan and Wideman, and would have expected such a salt to have herbicidal activity. Before the PTO may combine the disclosures of two or more prior art references in order to establish *prima facie* obviousness, there must be some sug

Page 1944

gestion for doing so, found either in the references themselves or in the knowledge generally available to one of ordinary skill in the art. *In re Fine*, 837 F.2d 1071, 1074, 5 USPQ2d 1596, 1598-99 (Fed. Cir. 1988). We see no such suggestion in Zorayan, which is directed to shampoo additives, nor in Wideman, which teaches that the amine used to make the claimed compound is a byproduct of the production of morpholine. Nor does the broad disclosure of Richter fill the gap, for the reasons discussed above.

Conspicuously missing from this record is any *evidence*, other than the PTO's speculation (if it be called evidence) that one of ordinary skill in the herbicidal art would have been motivated to make the modifications of the prior art salts necessary to arrive at the claimed 2-(2

'-aminoethoxy) ethanol salt. See *Grabiak*, 769 F.2d at 731-32, 226 USPQ at 872 ("[I]n the case before us there must be adequate support in the prior art for the [prior art] ester/ [claimed] thioester change in structure, in order to complete the PTO's *prima facie* case and shift the burden of going forward to the applicant."): *In re Lalu*, 747 F.2d 703, 705, 223 USPQ 1257, 1258 (Fed. Cir. 1984) ("The prior art must provide one of ordinary skill in the art the motivation to make the proposed molecular modifications needed to arrive at the claimed compound.")

### Conclusion

We conclude that the PTO did not establish a *prima facie* case of obviousness, and thus did not shift to Jones the burden of coming forward with unexpected results or other objective evidence of non-obviousness. Accordingly, the decision of the Board is  
**REVERSED.**

### Footnotes

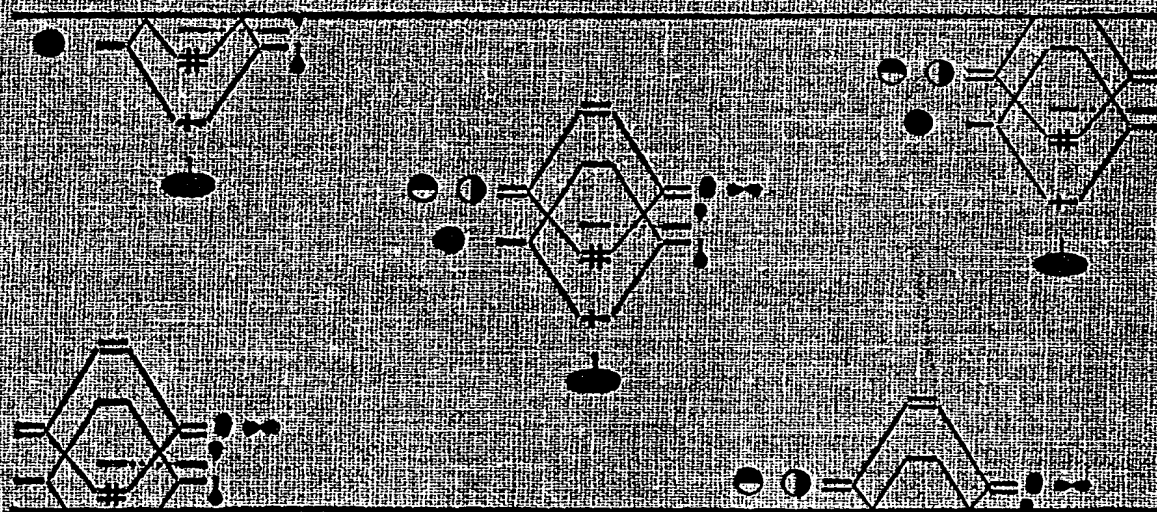


**BNA's Intellectual Property Library on CD -- Full Text of Cases (USPQ Second Series)**

Footnote 1. *See generally* Helmuth A. Wegner, "Prima Facie Obviousness of Chemical Compounds," 6 *Am. Pat. L. Assoc. O. J.* 271 (1978).

**- End of Case -**

# AB INITIO MOLECULAR ORBITAL THEORY



Warren J. Hehre  
Leo Radom  
Paul v.R. Schleyer  
John A. Pople

---

# AB INITIO MOLECULAR ORBITAL THEORY

---

**WARREN J. HEHRE**

*University of California, Irvine*

**LEO RADOM**

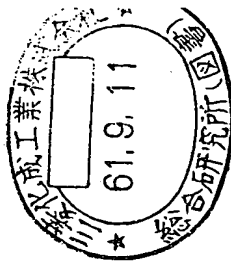
*Australian National University, Canberra*

**PAUL v. R. SCHLEYER**

*Universität Erlangen-Nürnberg, Erlangen, West Germany*

**JOHN A. POPL**

*Carnegie-Mellon University, Pittsburgh*



A Wiley-Interscience Publication

JOHN WILEY & SONS

To

NOKO, FAYE, INGE and JOY

Copyright © 1986 by John Wiley & Sons, Inc.

All rights reserved. Published simultaneously in Canada.

Reproduction or translation of any part of this work beyond that permitted by Section 107 or 108 of the 1976 United States Copyright Act without the permission of the copyright owner is unlawful. Requests for permission or further information should be addressed to the Permissions Department, John Wiley & Sons, Inc.

*Library of Congress Cataloging in Publication Data:*

Main entry under title:

Ab initio molecular orbital theory.

"A Wiley-Interscience publication."

Includes bibliographies and index.

1. Molecular orbitals.
  2. Quantum chemistry.
- I. Hehre, Warren J.

OD461.A185 1985 541.2'8 84-19524

ISBN 0-471-81241-2

atic comparison with experimental data. This aims to educate readers so that they can attach some level of confidence to computational results. Finally, Chapter 7 is an account of recent progress in some fields of chemistry where theory is making major contributions. The examples used are necessarily limited in scope and reflect particular interests of the authors but they should provide a reasonable overview of the current power of *ab initio* theory.

Certain omissions may be noted. No account is given of semiempirical, parameterized methods which parallel *ab initio* theories to some extent. Neither have we attempted to describe some recent more advanced quantum-mechanical methods such as multiconfigurational self-consistent-field theories. The emphasis is on those *ab initio* techniques which are well documented, easy to use, and readily available.

WARREN J. HEHRE  
LEO RADOM  
PAUL V.R. SCHLEYER  
JOHN A. POPL

Irvine, California  
Canberra, Australia  
Erlangen, West Germany  
Pittsburgh, Pennsylvania  
September 1985

## ACKNOWLEDGMENTS

Many people have contributed their ideas, the results of their research, and their time to this book during the eight years since its inception. The authors wish to express their gratitude to Jon Baker, Steve Binkley, Willem Bouma, Jayaraman Chandrasekhar, Tim Clark, Doug DeFrees, Kerwin Dobbs, Les Farnell, Michelle Franci, Mike Frisch, Peter Gill, Alan Hinde, Ken Houk, Bob Hout, Eluvathingal Jemmis, Scott Kahn, Elmar Kaufman, Michael Kausch, Alexander Kos, Bev Levi, Patty Pau, Bill Pietro, Steve Pollack, Krishnan Raghavachari, Noel Riggs, Cornelia Rohde, Svein Saezo, Berny Schlegel, Rolf Seeger, Guenther Spitznagel, Bob Whiteside, and Brian Yates for these contributions.

The drafts from which this book finally emerged were prepared by Meg Kessel, Sabrina Mullins, Denise Russell, Kathryn Severn, and Stacie Tibbetts. The drawings were skillfully executed by Arlene Saunders and the photographs prepared with the expert assistance of the staff of Irvine Photographics. Tom Hehre assisted greatly in the preparation of the index. To all of these people we express our sincere thanks. Finally, we acknowledge a large debt to Ross Nobes for his careful and thorough reading of the entire manuscript.

W. J. H.  
L. R.  
P. v. R. S.  
J. A. P.

# CONTENTS

|  |    |
|--|----|
| PROLOGUE   | 1  |
| 1. INTRODUCTION  | 5  |
| 1.1. Theoretical Models                                | 5  |
| 1.2. Molecular Orbital Models                          | 6  |
| 2. THEORETICAL BACKGROUND                              | 10 |
| 2.1. The Schrödinger Equation                          | 10 |
| 2.2. Separation of Nuclear Motion: Potential Surfaces  | 11 |
| 2.3. Atomic Units                                      | 13 |
| 2.4. Molecular Orbital Theory                          | 14 |
| 2.5. Basis Set Expansions                              | 17 |
| 2.6. Variational Methods and Hartree-Fock Theory       | 20 |
| 2.6.1. Closed-Shell Systems                            | 21 |
| 2.6.2. Open-Shell Systems                              | 22 |
| 2.6.3. Koopmans' Theorem and Ionization Potentials     | 24 |
| 2.7. Symmetry Properties                               | 24 |
| 2.8. Multiconfigurational Population Analysis          | 25 |
| 2.9. Multiple-Determinant Wavefunctions                | 29 |
| 2.9.1. Full Configuration Interaction                  | 32 |
| 2.9.2. Limited Configuration Interaction               | 34 |
| 2.9.3. Møller-Plesset Perturbation Theory              | 38 |
| 2.10. One-Electron Properties: Electric Dipole Moments | 40 |
| References   | 42 |

## 3. THE COMPUTATIONAL PROBLEM

- 3.1. Introduction 43
- 3.2. Logical Structure of the Computer Program 44
- 3.3. Computational Methods 50
  - 3.3.1. Methods for Integral Evaluation 51
  - 3.3.2. Methods for Solution of the Self-Consistent Equations 52
  - 3.3.3. Methods for Evaluation of the Energy Gradient 55
  - 3.3.4. Methods for Integral Transformation 56
  - 3.3.5. Use of Molecular Symmetry 58
  - 3.3.6. Methods for Generation of Three-Dimensional Molecular Orbital and Total Electron Density Plots 60

References 61

## 4. SELECTION OF A MODEL

- 4.1. Introduction 63
- 4.2. Hartree-Fock Methods 64
  - 4.2.1. Closed-Shell Determinantal Wavefunctions 64
  - 4.2.2. Open-Shell Determinantal Wavefunctions 64
- 4.3. Atomic Basis Sets of Gaussian Functions 65
  - 4.3.1. Minimal Basis Sets 66
    - a. STO-KG Minimal Basis Sets: The STO-3G Basis Set 68
  - 4.3.2. Extended *sp* Basis Sets 71
    - a. The 6-21G and 3-21G Split-Valence Basis Sets 76
    - b. Larger Split-Valence Representations: The 4-31G and 6-31G Basis Sets 79
  - 4.3.3. Polarization Basis Sets 80
    - a. The 6-31G\* and 6-31G\*\* Polarization Basis Sets 82
    - b. Larger Polarization Basis Sets. The 6-311G\*\* Basis Set for Use with Correlated Wavefunctions 82
  - 4.3.4. Efficient Basis Sets for Hypervalent Molecules 83
    - a. The 3-21G(\*) Basis Set for Second-Row Elements 84
  - 4.3.5. Basis Sets Incorporating Diffuse Functions 86
    - a. The 3-21+G, 3-21+G(\*) and 6-31+G\* Basis Sets 86
  - 4.3.6. Relative Computational Times of Hartree-Fock Models with Gaussian Basis Sets 88
- 4.4. Electron Correlation Methods 88
  - 4.4.1. Limited Configuration Interaction 89
  - 4.4.2. Møller-Plesset Perturbation Treatments 90
  - 4.4.3. Relative Computational Times of Correlation Methods 90
- 4.5. Molecular Geometry 91
  - 4.5.1. Standard Molecular Geometries 92
  - 4.5.2. Partial Optimization of Molecular Geometry 93

63

- 4.5.3. Complete Optimization of Molecular Geometry 94
- 4.5.4. Use of Geometries from Lower Theoretical Levels 95
- 4.6. Nomenclature 96
- 4.7. Conclusion 97
- References 98

## 5. PRACTICAL CONSIDERATIONS: INPUT AND OUTPUT

- 5.1. Introduction 101
- 5.2. Input: The Z-Matrix 101
  - 5.2.1. A Simple Triatomic: Water 104
  - 5.2.2. A Tetraatomic Chain: Hydrogen Peroxide 106
  - 5.2.3. Branched Structures: Fluoromethane 107
  - 5.2.4. Larger Systems 107
  - 5.2.5. The Use of Dummy Atoms 108
  - 5.2.6. Optimization of Molecular Geometry 111
- 5.3. Output 113
  - 5.3.1. STO-3G Calculation on Formaldehyde 114
  - 5.3.2. 3-21G Calculation on Formaldehyde 118
  - 5.3.3. 6-31G\* Calculation on Ammonia Oxide 118
  - 5.3.4. Graphical Representation of Molecular Orbitals and Electron Densities 125
- 5.4. Archival Storage 125
- References 131

## 6. THE PERFORMANCE OF THE MODEL

- 6.1. Introduction 133
- 6.2. Equilibrium Geometries 135
  - 6.2.1. Sources of Error in the Comparison of Theoretical and Experimental Equilibrium Geometries 137
  - 6.2.2. Structures of  $\text{AH}_n$  Molecules 137
    - a. Hartree-Fock Structures 137
    - b. Effect of Electron Correlation on the Structures of  $\text{AH}_n$  Molecules 142
  - 6.2.3. Structures of Two-Heavy-Atom Molecules 146
    - a. Hartree-Fock Structures 146
    - b. Effect of Electron Correlation on Structures of Two-Heavy-Atom Molecules 155
  - 6.2.4. Structures of Larger Molecules 164
    - a. Equilibrium Bond Lengths 165
    - b. Skeletal Bond Angles 175
  - 6.2.5. Structures of Hypervalent Molecules 181
  - 6.2.6. Structures of Molecules Containing Third- and Fourth-Row Main-Group Elements 187
  - 6.2.7. Structures of Transition-Metal Inorganics and Organometallics 187

133

- (i) Use of Isogyric Reactions 275
- (ii) Extension of Treatment of Electron Correlation 276
- (iii) Improvement of the Hartree-Fock Basis Set 277
- c. AB Single-Bond Energies 277
- 6.5.3. Energies of Hydrogenation Reactions 279
  - a. Two-Heavy-Atom Molecules 280
  - b. Hypervalent Molecules 285
  - c. Effect of Electron Correlation on Hydrogenation Energies 285
- 6.5.4. Energies of Reactions Relating Multiple and Single Bonds 288
- 6.5.5. Relative Energies of Structural Isomers 290
- 6.5.6. Energies of Isodesmic Reactions 298
  - a. Bond Separation Reactions 300
  - b. Calculation of Heats of Formation 307
- 6.5.7. Energies of Hydrogen-Transfer Reactions 308
- 6.5.8. Energies of Proton-Transfer and Related Reactions 310
  - a. Absolute Acidities and Basicities 310
  - b. Effect of Electron Correlation on Absolute Basicities 314
  - c. Relative Acidities and Basicities 314
  - d. Effect of Remote Substituents on Acid and Base Strength 317
  - e. Lithium Cation Affinities 319
- 6.5.9. The Additivity of Basis Set and Electron Correlation Effects in Estimating Relative Energies 321
- 6.5.10. Concluding Remarks and Recommendations 323
- 6.6. Electric Dipole Moments and Molecular Charge Distributions 324
  - 6.6.1. Electric Dipole Moments 324
    - a. Diatomic and Small Polyatomic Molecules 325
    - b. Hydrocarbons 327
    - c. Compounds Containing Heteroatoms 330
    - d. Substituted Benzenes 330
    - e. Hypervalent Molecules 331
    - f. Effect of Electron Correlation on Electric Dipole Moments 331
  - 6.6.2. Molecular Charge Distributions 336

References 341

## 7. APPLICATIONS OF THE THEORY

345

- 7.1. Introduction 345
- 7.2. Intramolecular Interactions 346
  - 7.2.1. Interactions Between Directly-Bonded Groups 346

- 6.2.8. Structures of Short-Lived Reactive Species 193
  - a. Open-Shell Systems: Free Radicals 194
  - b. Carbenes and Related Compounds 204
  - c. Anions 204
  - d. Cations 208
- 6.2.9. Structures of Intermolecular Complexes 212
  - a. Donor-Acceptor Complexes 213
  - b. Metal-Carbonyl Complexes 213
  - c. Hydrogen-Bonded Complexes 215
- 6.2.10. Improved Structural Predictions 224
- 6.2.11. Concluding Remarks and Recommendations 226
- 6.3. Vibrational Frequencies and Thermodynamic Properties 228
  - 6.3.1. Calculation of Harmonic Vibrational Frequencies 228
  - 6.3.2. Sources of Error in Comparison of Theoretical and Experimental Vibrational Frequencies 229
  - 6.3.3. Frequencies of Diatomic Molecules 231
  - 6.3.4. Frequencies of One-Heavy-Atom Hydrides 233
  - 6.3.5. Frequencies of Two-Heavy-Atom Hydrides 236
  - 6.3.6. Frequencies of Larger Polyatomic Molecules 246
  - 6.3.7. Frequencies of Molecules Poorly Represented by Conventional Valence Structures 246
  - 6.3.8. Isolated CH Stretching Frequencies 250
  - 6.3.9. Calculation of Thermodynamic Properties 251
    - a. Entropies 251
    - b. Equilibrium Isotope Effects 252
    - c. Temperature and Zero-Point-Energy Corrections to Experimental Thermochemical Data 258
- 6.3.10. Concluding Remarks and Recommendations 260
- 6.4. Molecular Conformations and Barriers to Rotation and Inversion 261
  - 6.4.1. Completely Optimized Rotors and Invertors 262
    - a. Rotational Barriers 263
    - b. Inversion Barriers 265
    - c. Effect of Electron Correlation on Rotation and Inversion Barriers 266
    - d. Conformational Isomers 267
  - 6.4.2. Rigid-Rotor Approximation 269
    - a. Rotational Barriers 269
    - b. Remote Substituent Effects 270
- 6.5. Thermochemical Stabilities of Molecules 270
  - 6.5.1. Sources of Error in Comparisons of Theoretical and Experimental Relative Thermochemical Stabilities 272
  - 6.5.2. Bond Dissociation Energies 273
    - a. AH Bond Energies 273
    - b. Improved Calculations of  $\text{CH}_n$  Bond Dissociation Energies 275



- a. Stabilization of Carbocations 350
- b. Stabilization of Radicals 351
- c. Stabilization of Carbanions 351
- d. Stabilization of Singlet and Triplet Carbenes 352
- e. Stabilization of Larger Systems 353
- f. Methyl Stabilization Energies for Amines, Alcohols and their Protonated and Deprotonated Forms: Effects of Substituents on the Acid and Base Strengths of Nitrogen and Oxygen Compounds 354
- 7.2.2. Bond Separation Reactions and Geminal Interactions 356
  - a. Interactions in  $X-CH_2-Y$  357
  - b. Structural Consequences of Geminal Interactions 359
- 7.2.3. Interactions in Aromatic Systems 360
  - a. Disubstituted Benzenes 360
  - b. Analysis of Gas-Phase Acidities and Basicities 362
  - c. Torsional Barriers in *para*-Substituted Phenols 365
  - d. Proton Affinities of Alkyl Benzenes 367
  - e. Sites of Protonation in Substituted Benzenes 367
- 7.2.4. Aromaticity 370
  - a. Hydrocarbons and Hydrocarbon Ions 370
  - b. Benzene and Pyridine Analogues 373
  - c. Aromaticity in Three Dimensions 375
- 7.3. Reactive Intermediates 378
  - 7.3.1. Carbocations and Carbodications 379
    - a. Protonated Alkanes 380
      - (i) Protonated Methane 381
      - (ii) Protonated Ethane 382
    - b. Protonated Acetylene and Ethylene: Hydrogen Bridging in Simple Carbocations 383
      - (i) Protonated Acetylene: The Vinyl Cation 383
      - (ii) Protonated Ethylene: The Ethyl Cation 384
    - c. Larger Systems 385
      - (i)  $C_3H_5^+$  385
      - (ii)  $C_3H_7^+$  388
      - (iii)  $C_4H_7^+$ , The Cyclopropylcarbanyl and Cyclobutyl Cations,  $C_4H_9^+$ , The Methylcyclopropylcarbanyl and Methylcyclobutyl Cations 390
      - (iv)  $C_4H_9^+$ , The Secondary Butyl Cation 394
      - (v)  $C_6H_7^+$ , Protonated Benzene 396
    - d. Carbodications 396
      - (i) The Methane Dication 397
      - (ii) The Ethane Dication 398
      - (iii) The Cyclobutadiene Dication 399
      - (iv) Dihydrodiborele and Other Analogues of the Cyclobutadiene Dication 400

- 7.3.2. Carbanions and Polar Organometallics: 401
  - a. Methylolithium and Other Analogues of Methyl Anion 402
  - b. Alkali Metal and Alkaline Earth Analogues of Larger Carbanions 406
- 7.3.3. Carbenoids 414
  - a. Reactions of Carbenoids with Olefins 420
  - b. Metal Carbenes as Methylene Transfer Agents: The Role of the Tebbe Reagent in Olefin Metathesis 423
- 7.4. Violation of Conventional Structure Rules 425
  - 7.4.1. Planar Tetracoordinate Carbon 428
    - a. Stereochemistry of Methane Analogues 432
    - b. Structure of the Tebbe Reagent 436
  - 7.4.2. Other Violations of Van't Hoff Stereochemistry. Doubly-Bridged Acetylenes and Perpendicular Ethylenes 438
  - 7.4.3. Structures of Transition-Metal Carbenes and Transition Metal Alkyls. The Role of Hyperconjugation in Carbon-Metal Bonding 445
- 7.5. Molecules with Several Metals 450
  - 7.5.1. Lithiocarbons and Lithiated Hydrocarbons 450
    - a. 1,2-Dithioethane and Higher  $\alpha, \omega$ -Dithioalkanes 451
    - b. Dithioethylene 454
    - c. Lithiocarbons 456
      - (i)  $CLi_5$  and  $CLi_6$  458
      - (ii)  $C_3Li_4$  458
      - (iii)  $C_4Li_4$  461
  - 7.5.2. Small Beryllium Clusters 463
- 7.6. Reaction Potential Surfaces 466
  - 7.6.1. Classification of Reaction Types 467
    - a. Isomerizations 467
    - b. Addition or Combination Reactions 468
    - c. Bimolecular Transfer Reactions 469
    - d. Reaction Profiles 469
  - 7.6.2. Computational Procedures 470
  - 7.6.3. Reaction Surfaces for Two-Heavy Atom Systems 471
    - a.  $C_2H_2$  473
    - b.  $CHN$  473
    - c.  $C_2H_4$  474
    - d.  $CH_3N$  476
    - e.  $CH_2O$  477
    - f.  $N_2H_2$  478
    - g.  $CH_3N$  479
  - 7.6.4. Reaction Surfaces for Small Cationic Systems 480

- a.  $\text{HOC}^+$ : A New Interstellar Molecule 481
- b. The Nature of the Methoxy Cation 483
- c. The Methylenoxonium Radical Cation,  $\text{CH}_2\text{OH}_2^+$ , and Related Systems 484
- d.  $\text{C}_2\text{H}_3\text{O}^+$  486
- 7.6.5. Reaction Mechanisms 490
  - a. Mechanistic Aspects of Gas- and Solution-Phase  $\text{S}_{\text{N}}2$  Reactions 491
  - b. Stereochemistry of Addition to Alkenes 494
  - c. 1,3- and 1,5-Sigmatropic Rearrangements. Symmetry-Allowed and Symmetry-Forbidden Processes 501

References 504

EPILOGUE

523

INDEX

525

# PROLOGUE

*The more progress physical sciences make, the more they tend to enter the domain of mathematics, which is a kind of centre to which they all converge. We may even judge the degree of perfection to which a science has arrived by the facility with which it may be submitted to calculation [1].*

*Adolphe Quetelet 1796-1874*

This book helps to document the extent to which chemistry may now "be submitted to calculation."

The key to theoretical chemistry is molecular quantum mechanics. This is the science relating molecular properties to the motion and interactions of electrons and nuclei. Soon after its formulation in 1925 [2], it became clear that solution of the Schrödinger differential equation could, in principle, lead to direct quantitative prediction of most, if not all, chemical phenomena using only the values of a small number of physical constants (Planck's constant, the velocity of light, and the masses and charges of electrons and nuclei). Such a procedure constitutes an *ab initio* approach to chemistry, independent of any experiment other than determination of these constants. It was also early recognized that solution of the Schrödinger equation was a formidable if not completely impossible mathematical problem for any but the very simplest of systems.

*The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to calculations much too complicated to be soluble [3].*

*P.A.M. Dirac 1902-1984*

In practice, the Schrödinger equation has to be replaced by approximate mathematical models for which the possibility of solution exists. The advent of powerful digital computers and of increasingly efficient computer programs has led to significant progress in recent years, both in the development of ever more sophisticated approximate quantum mechanical models and in the application of these models to problems of chemical significance. It is fair to say that theory has now advanced sufficiently far as to provide the chemist with an alternative independent approach to his subject.

It is unlikely that chemistry will change overnight from an experimental, to a theoretical science. Much of what now forms its basis may not be subjected to calculation, at least not at present. Nevertheless, it is reasonable to anticipate that an increasing number of chemical investigations which might previously have been performed experimentally will instead be carried out on a digital computer. A number of factors will be responsible for this change in strategy. In many respects theoretical calculations already are more powerful than experiment. They are not bound by practical considerations. Any chemical species may be scrutinized theoretically; calculations on cations, anions, and other reactive intermediates, which might be difficult to investigate experimentally, pose, in principle, no greater problem than calculations carried out on more stable and easily observed molecules. Detailed information about reaction transition structures, excited states, as well as on hypothetical molecular arrangements, deformed molecules, for example, may only be obtained by computation. Calculations are easy to perform and involve little human time and effort relative to the large amount of information obtained. They are becoming less and less costly, whereas experimental work is ever more expensive. Minicomputers, available at a price less than that of a double-focusing mass spectrometer or a research nuclear magnetic resonance instrument, are capable of performing all the calculations described in this book. Expense may well be the decisive factor in determining how investigations are to be carried out in the future.

The quantification of chemistry may not be welcomed by all. Thus,

*Every attempt to employ mathematical methods in the study of chemical questions must be considered profoundly irrational and contrary to the spirit of chemistry. If mathematical analysis should ever hold a prominent place in chemistry—an aberration which is happily almost impossible—it would occasion a rapid and widespread degeneration of that science [4].*

A. Comte 1798-1857

Even today many chemists are uncomfortable with the thought of using a digital computer as an investigative tool. Many are skeptical. Some are uninformed or even prejudiced. They do not believe that theory is capable of making accurate predictions of chemical phenomena. Some may feel that the theoretical methods are too difficult to learn, let alone apply. One of the primary goals of this book is to help overcome these reservations, and show the extent to which theoretical calculations, in their present stage of development, can be employed as a practical means of doing chemistry.

Although theory will continue to help understand in more detail systems that

have already been investigated experimentally, an exciting prospect is the exploration of new areas of chemistry. Such areas are remarkably large; the vast majority of chemistry remains to be discovered if one considers the whole of the periodic table! Computational work enables the investigator to scrutinize quickly large numbers of seemingly reasonable molecules about which little or nothing may be known. Calculations can help to indicate whether such species are of sufficient interest to justify their preparation and examination, and whether they will be sufficiently stable to make experimental investigation practical. In many instances, the information available theoretically may suffice to answer questions of interest; there may be no need to carry out confirmatory experimental studies. This book describes some of the progress made by theory in "discovering" new chemistry.

## REFERENCES

1. A. Quetelet, *Instructions Populaires sur le Calcul des Probabilités*, Tatlier, Brussels, 1828, p. 230.
2. E. Schrödinger, *Ann. Phys.*, 79, 361 (1926).
3. P. A. M. Dirac, *Proc. Roy. Soc. (London)*, 123, 714 (1929).
4. A. Comte, *Philosophie Positive*, 1830.

# INTRODUCTION

## 1.1. THEORETICAL MODELS

Two broadly different conceptual approaches to the approximate solution of the Schrödinger equation are possible. In the first, each problem is examined at the highest level of theory currently feasible for a system of its size. Very small systems, such as the helium atom or the hydrogen molecule, can clearly be handled at much higher levels of precision than are feasible for systems containing, say, a hundred or more electrons. In the second approach, with which this book is primarily concerned, a level of theory is first clearly defined after which it is applied *uniformly* to molecular systems of *all* sizes up to a maximum determined by available computational resources. Such a theory, if prescribed uniquely for any configuration of nuclei and any number of electrons, may be termed a *theoretical model*, within which all structures, energies, and other physical properties can be explored once the mathematical procedure has been implemented through a computer program. A *theoretical-model chemistry* results. The model may be *tested* by *systematic* comparison of its findings with known experimental results. If comparisons prove favorable, the model acquires some predictive value in situations where experimental data are unavailable. A number of theoretical models are described in this book, and their range of applicability, their successes, and their failures are thoroughly documented.

A theoretical model should possess a number of important characteristics. First, it should be both *unique* and *well defined*. The procedure for obtaining an energy and a wavefunction as an approximate solution of the Schrödinger equation should

be completely specified in terms of nuclear positions and the number and spins of the electrons in the molecule. A second desirable feature is *continuity*: all *potential surfaces* should be continuous with respect to nuclear displacements. Special procedures must not be used for symmetrical molecules which might lead to results which are discontinuous with those for structures in which the nuclei are slightly displaced to nonsymmetrical positions. A theoretical model should also be *unbiased*. No appeal to "chemical intuition" should be made in setting up the details of the calculation. For example, while calculations in which electrons are assigned to certain "bond orbitals" might be satisfactory for many molecules, they are not suitable for those nuclear configurations where the locations of "bonds" are apt to be ambiguous. A theory can only be used for the analysis of such concepts as bonding if pre-suppositions have not been built into its formulation.

Another important requirement for a satisfactory theoretical model is *size-consistency*: relative errors involved in a calculation should increase more or less in proportion to the size of the molecule. This is particularly important if the model is to be used in a comparative manner, relating properties of molecules of different sizes. While it is generally not possible to satisfy this condition fully, it is often possible to construct models that are *size-consistent for infinitely separated systems*. This means that application of the model to a system of several molecules at infinite separation will yield properties that equal the sum of these same properties for the individual molecules.

It is also desirable that a theoretical model be *variational*, that is, yield a total energy that is an *upper bound* to that which would result from exact solution of the full Schrödinger equation.

Finally, a practical theoretical model should be capable of implementation on a computer and be usable with minimal human and computational effort. This enables application of the model to extensive exploration of the properties of a large number of molecules. The development of efficient programs for such models is a major area of research in present-day theoretical chemistry.

## 1.2. MOLECULAR ORBITAL MODELS

The theoretical models discussed in this book are all based on *molecular orbital (MO) theory*. This approximates treatment of electron distribution and motion assigns individual electrons to one-electron functions termed *spin orbitals*. These comprise a product of spatial functions, termed *molecular orbitals*,  $\psi_1(x, y, z)$ ,  $\psi_2(x, y, z)$ ,  $\psi_3(x, y, z)$ , . . . , and either  $\alpha$  or  $\beta$  *spin components*. The spin orbitals are allowed complete freedom to spread throughout the molecule, their exact form being determined variationally to minimize the total energy. In the simplest version of the theory, a single assignment of electrons to orbitals (sometimes called an *electron configuration*) is made. These orbitals are then brought together to form a suitable *many-electron wavefunction*  $\Psi$  which is the simplest MO approximation to the solution of the Schrödinger equation.

In practical calculations, the molecular orbitals  $\psi_1, \psi_2, \dots$  are further restricted

## MOLECULAR ORBITAL MODELS

to be linear combinations of a set of  $N$  known one-electron functions  $\phi_1(x, y, z)$ ,  $\phi_2(x, y, z)$ , . . . ,  $\phi_N(x, y, z)$ :

$$\psi_I = \sum_{\mu=1}^N c_{\mu I} \phi_{\mu} \quad (1.1)$$

The functions  $\phi_1, \phi_2, \dots, \phi_N$  (which are defined in the specification of the model) are known as *one-electron basis functions*, or simply as *basis functions*. They constitute the *basis set*. If the basis functions are the *atomic orbitals* for the atoms making up the molecule, Eq. (1.1) is often described as the *linear combination of atomic orbitals (LCAO) approximation*, and is frequently used in qualitative descriptions of electronic structure.

Given the basis set, the unknown coefficients  $c_{\mu I}$  are determined so that the total electronic energy calculated from the many-electron wavefunction is minimized and, according to the *variational theorem*, is as close as possible to the energy corresponding to exact solution of the Schrödinger equation. This energy and the corresponding wavefunction represent the best that can be obtained within the *Hartree-Fock approximation*, that is, the best given the constraints imposed by: (a) the use of a limited basis set in the orbital expansion, and (b) the use of a single assignment of electrons to orbitals.

Hartree-Fock models are the simplest to use for chemical applications and have been employed in many of the studies carried out to date. To specify the model in full, it is only necessary to define a unique basis set  $\phi_1, \phi_2, \dots, \phi_N$  for any nuclear configuration. This is conveniently done by having a standard set of basis functions for each nucleus, centered at the nuclear position, which depend only on the corresponding atomic number. Thus, there would be a set of functions for each hydrogen atom and other sets for each carbon and so forth. In the simplest Hartree-Fock models, the number of basis functions on each atom will be as small as possible, that is, only large enough to accommodate all the electrons and still maintain spherical symmetry. As a consequence, the molecular orbitals (1.1) will have only limited flexibility. If larger basis sets are used, the number of adjustable coefficients in the variational procedure increases, and an improved description of the molecular orbitals is obtained. Very large basis sets will result in nearly complete flexibility. The limit of such an approach, termed the *Hartree-Fock limit*, represents the best that can be done with a single electron configuration. As is shown in later chapters, theoretical-model chemistry at the Hartree-Fock limit has become fairly well characterized, and many of its successes and limitations are now well documented.

The main deficiency of Hartree-Fock theory is its incomplete description of the *correlation* between motions of the electrons. Even with a large and completely flexible basis set, the full solution of the Schrödinger equation cannot be expressed in terms of a *single electron configuration*, that is, a unique assignment of electrons to orbitals. To correct for such a deficiency, it is necessary to use wavefunctions that go beyond the Hartree-Fock level, that is, that represent more than a single electron configuration. If  $\Psi_0$  is the full Hartree-Fock many-electron wavefunction,

## MOLECULAR ORBITAL MODELS

tion with a completely flexible basis set. Notice that the two directions on this chart correspond precisely to the two approximations which have been made in order to replace the full Schrödinger equation by practical molecular orbital schemes capable of application to diverse systems. Progression in the vertical direction ("Improvement of Basis Set") corresponds to increasing flexibility of the one-electron spin orbitals [Eq. (1.1)]. Progression in the horizontal direction ("Improvement of Correlation Treatment") corresponds to improved flexibility arising from taking the sum of an increasing number of many-electron functions [Eq. (1.2)]. It follows, therefore, that the bottom right-hand corner of the diagram constitutes the exact solution of the nonrelativistic Schrödinger equation.

The main objective of this book is to describe and to document the performance of a number of theoretical models which comprise such an investigation chart. Many of the applications to date have been at the Hartree-Fock level (left-hand column in Figure 1.1); this is reflected in the coverage of subsequent chapters. However, sufficient investigations have now been carried out beyond Hartree-Fock to enable some assessment of the performance of such theoretical models.

|                               |                          |              |                                      |                                |  |
|-------------------------------|--------------------------|--------------|--------------------------------------|--------------------------------|--|
| Completely Flexible Basis Set | Improvement of Basis Set | Hartree-Fock | Improvement of Correlation Treatment | Full Configuration Interaction | Exact Solution of Schrödinger Equation |
|-------------------------------|--------------------------|--------------|--------------------------------------|--------------------------------|--|

**FIGURE 1.1.** Schematic representation of theoretical models showing basis set improvement vertically and correlation improvement horizontally.

the extended approximate form for the more accurate wavefunction  $\Psi$  is

$$\Psi = a_0 \Psi_0 + a_1 \Psi_1 + a_2 \Psi_2 + \dots. \quad (1.2)$$

Here  $\Psi_1, \Psi_2, \dots$  are wavefunctions for other configurations, and the linear coefficients  $a_0, a_1, \dots$  are to be determined. Inclusion of wavefunctions for all possible alternative electron configurations (within the framework of a given basis set) is termed *full configuration interaction*. It represents the best that can be done using that basis set. Practical methods, which may be sequenced in order of increasing sophistication and accuracy, seek either to limit the number of configurations or to approximate the effect which their inclusion has on the total wavefunction.

The two directions in which theoretical models may be improved can be shown with a two-dimensional chart as in Figure 1.1. The simplest type of model is a Hartree-Fock treatment using a small basis set. This would be placed at the top left of the diagram. As more sophisticated models are applied, an investigation may move downwards (improvement of the basis set) or from left to right (improvement of correlation technique). The bottom row, which may not be realizable in practice, represents various methods using a completely flexible basis. The right-hand column, which may also be impractical, represents full configuration interaction with a given basis. The bottom right-hand corner corresponds to full configuration interaction.